

SCORCH PREVENTION IN FLEXIBLE POLYURETHANE FOAMS

Field of the Invention

The present invention relates to the prevention of discoloration in flexible polyurethane foams, a phenomenon commonly referred to as "scorching". More particularly, the invention relates to novel compositions useful to alleviate or prevent the aforementioned undesirable effect.

Background of the invention

Scorching is an undesirable discoloration phenomenon which occurs within the foam blocks, causing them to assume a yellow to brown color. This discoloration is especially apparent in the center of the blocks where the internal temperatures remain high for a relatively long period of time. The exposure of the interior of the foams to high temperatures leads to embrittlement and the core discoloration commonly known as scorching. In extreme cases this can result in ignition of the foam buns, sometimes with disastrous consequences. In some severe cases, it can cause a degradation of physical properties or, where scorching is particularly intense, can result in spontaneous combustion of freshly made foam blocks. Flame retardants, with few exceptions, e.g., pentabromodiphenyl oxide, exacerbate the "scorch" problems that arise during processing of low density foams.

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It is known that the use of flame retardants (FR) in polyols can lead to even higher discoloration in polyurethane (PU) foams than the non FR grades. Flame retardants, with few exceptions, create two major problems for the manufacturers of water-blown, flexible, slab stock foam. They increase the "scorch" problems that arise during processing of low density foams and they increase the smoldering tendency of foams subjected to the California TB 117 standard.

The flame-retardant tribromoneopentyl alcohol (known as FR-513 ex Dead Sea Bromine Group (DSBG)) was investigated as flame retardant in PU foams already in 1975 [J. H. Botkin, Scorch Inhibitors for Polyurethane Slabstock Foams, *Adv. Urethane Sci. Technol.*, vol. 14, pp. 57-80, 1998].

The use of antioxidants has been proposed in the art and it can mitigate to some extent the increased scorch and discoloration in flame retarded polyols and foams. However, the literature consulted, and experiments carried out, by the inventors indicate that antioxidants by themselves are not very efficient in preventing scorch when halogen containing flame retardants, are present in the formulation. Thus, the art has so far failed to provide an efficient solution to the problem of scorch taking place during the manufacturing of flexible polyurethane foams.

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It is an object of the present invention to provide an anti-scorch composition that efficiently addresses the problem of scorch for flexible polyurethane formulations flame retarded with halogen-containing flame retardants.

It is another object of the invention to provide an anti-scorch combination that overcomes the drawbacks of the prior art.

It is yet another object of the invention to provide a method for preventing or diminishing the occurrence of scorch during the manufacturing of flexible polyurethane foams.

Other purposes and advantages of the invention will become apparent as the description proceeds.

Summary of the invention

The invention is directed to an anti-scorch composition for flame-retarded flexible polyurethane foams, comprising, in combination, one or more antioxidant agents, together with one or more salt(s) of an organic acid.

According to a preferred embodiment of the invention the organic acid is selected from among saturated or unsaturated, aliphatic or aromatic mono- or di-carboxylated acids. According to another preferred embodiment of the invention the salt of the organic acid is a salt of Ca, Zn, Ba or Sn.

Illustrative and non-limitative examples of antioxidant agents are phenols and amino oxygen scavengers, such as hindered phenols.

Illustrative and non-limitative examples of amino oxygen scavengers include alkylated diphenylamines.

According to a preferred embodiment of the invention the flame-retardant is a halogen-containing flame retardant, such as – but not limited to – tribromoneopentyl alcohol.

According to a further preferred embodiment of the invention the composition further comprises an epoxy compound, such as – but not limited to – diglycidyl ether of bisphenol A and its derivatives.

In another aspect the invention is directed to a method for preventing or diminishing scorch in flame-retarded flexible polyurethane foams, comprising adding to the polyurethane composition, prior to foaming, one or more antioxidant agents, together with one or more salt(s) of an organic acid, as hereinbefore defined.

The above and other objects and advantages of the invention will be better understood from the following illustrative and non-limitative examples.

Test Procedure:**MW test protocol for scorch evaluation**

The test method consists of the following steps:

1. Foam production in a small shoe box with a square cross-section
2. Immediately after the foam rise is complete (usually less than 2 minutes), the foam is heated using a microwave (MW) oven using a predetermined time and power level.
3. The foam is then heated in an oven at $120\pm2^\circ\text{C}$ for 2 min.
4. The foam is allowed to cure at RT (room temperature) for an additional 15 min.
5. By the end of the RT curing time the foam is cut and the scorch is observed.

Scorch evaluation

The scorch is evaluated using two methods:

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1. The foam is photographed using a digital camera. This allows for a visual comparison between the scorch of a reference formulation and the scorch of the formulation under investigation.
2. The foam color is analyzed using a spectrophotometer. The results are expressed in the usual color space: L*a*b and performed accordingly to ASTM D-2244.

Note: the scorch intensity may change from day to day according to the physical conditions of the surroundings in which the foam has been prepared (usually the temperature and relative humidity). This is why it is customary to prepare each day a reference sample.

Example

Foam preparation

The mixture was prepared in a 0.65 l disposable cup. The components were added one at a time starting with the polyol. The mixture was vigorously mixed at 3500 rpm for 10 seconds following the addition of each component, not including the Toluene diisocyanate (TDI). After the addition of TDI, the mixture was mixed for an additional 10 sec and then poured into a 25X25X17 cm cardboard box. The times between the TDI addition and the pouring into the cardboard box and the end of the foam blowing (rise time) were monitored.

Comparative Samples and Results

The effect of the antiscorching ingredients and their combinations was measured on the darkest areas on the foam after microwave oven treatment, using a spectrophotometer which provides color measurements expressed in the L*a*b color space. The most relevant color parameters for scorch assessment are Δb and ΔE .

The color parameters are given as normalized values relative to the reference specimens. As explained in the MW oven procedure, this particular method for scorch propensity assessment requires that a new reference foam be prepared, subjected to MW oven procedure and measured in each and every day of measurements. This requirement is related to the effect various experimental conditions, such as the temperature and the relative humidity of the air in the lab may have on the level of scorch. The normalized Δb and ΔE differences between the reference foam (containing no antiscorching ingredients) and foams containing various ingredients with antiscorch effects, are calculated as follows:

$$\Delta\Delta b(\text{normalized}) = \frac{\Delta b(\text{reference}) - \Delta b(\text{sample})}{\Delta b(\text{reference})} \cdot 100$$

$$\Delta\Delta E(\text{normalized}) = \frac{\Delta E(\text{reference}) - \Delta E(\text{sample})}{\Delta E(\text{reference})} \cdot 100$$

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Note: a value greater than 100 can sometimes emerge from these calculations since both Δb and ΔE for each specimen are compared to a factory white standard. The higher the $\Delta\Delta b$ and $\Delta\Delta E$ values, the lower the scorch.

Formulations for two grades of foams are shown in Tables I and II: Medium density foams (Table I) have a density of approximately 25 Kg/m³; Low density foams (Table II) have a density of approximately 15 Kg/m³.

Ingredients: AO1 and AO5 are antioxidants produced by Goldschmidt (Degussa) and contain combinations of hindered phenols and aromatic diamines.

Epoxy 828 is Diglycidyl ether of bisphenol A (DGEBA).

ESBO = Epoxidized Soya Bean oil.

All other ingredients below the FR-513 line in the table are metallic salts (Ca, Zn, Ba, Ti) of organic acids.

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Table I
Normal density foams

Ingredient	1	2	3	4	5	6	7	8	9
Polyol	100	100	100	100	100	100	100	100	100
Water	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Silicon 8228	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Amine Dabco 33LV	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Amine BDE	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Tin T-9	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Toluene di-isocyanate (TDI)	56.31	56.31	56.31	56.31	56.31	56.31	56.31	56.31	56.31
FR-513	5	5	5	5	5	5	5	5	5
AO5	0.42	0.21	0.85						
Calcium stearate (CaSt)	0.42	0.21							
PK4610	0.42	0.21							
Epoxy 828			0.85		0.1	0.1	0.21		
ESBO				1.7					
LZB 138					0.21			0.21	0.21
AO 1					0.21	0.21	0.21	0.21	0.21
CZ400						0.21		0.21	
CZ 118 S							0.21		0.21
ΔΔb	90.13	106.1	49.17	-132.6	82.32	77.06	93.93	84.58	102.9
ΔΔE	17.04	10.84	18.34	-99.43	27.61	32.67	30.14	37.42	33.98

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Table II
Low density foams

Ingredient	1	2	3	4	5	6
Polyol	100	100	100	100	100	100
Water	5.25	5.25	5.25	5.25	5.25	5.25
Silicon 8228	1.0	1.0	1.0	1.0	1.0	1.0
Amine Dabco 33LV	0.06	0.06	0.06	0.06	0.06	0.06
Amine BDE	0.046	0.046	0.046	0.046	0.046	0.046
Tin T-9	0.37	0.37	0.37	0.37	0.37	0.37
Methylene Chloride (MeCl)	11	11	11	11	11	11
TDI	71.1	71.1	71.1	71.1	71.1	71.1
FR-513	15	15	15	15	15	15
AO5			0.1	0.3		0.2
Epoxy 828	0.5	1.0				
BM270					1.0	0.2
LZB287						0.6
ΔΔb	-14.11	24.37	-15.10	-77.1	95.29	50.90
ΔΔE	0	13.73	-10.13	-41.03	27.80	11.70

From the results in Tables I and II it is clearly seen that the compositions of the invention attain a substantial improvement.

The notations and composition of materials used as antiscorch ingredients in the examples in Tables I and II are detailed in Table III.

Table III - Composition of ingredients used as antiscorch materials

Producer	Name	Ingredients	State
Akros	Lankromark LZB287	1) Barium oleate Barium t-butylbenzoate	40%
		2) Zinc 2-ethylhexanoate	5-10%
		3) Phosphite esters	20-40%
		4) 2-(2-butoxyethoxy) ethanol	5-10%
		5) Phenol	5-10%
	Lankromark LZB413	1) Barium 2-ethylhexanoate Barium oleate Barium t-butylbenzoate	20%
		2) Zinc 2-ethylhexanoate	1-5%
		3) Zinc t-butylbenzonoate	1-5%
		4) Phosphite esters	20-40%
		5) Trisnonylphenyl phosphite	1-5%
		6) 2-(2-butoxyethoxy ethanol)	
	Lankromark LZB138	1) Barium compounds (% as barium metal)	2-15%
		2) Phenol	1-5%
	Lankroflex E2307	1) Epoxidised soya bean oil	> 99%
	Tinstab BTS71S	1) n-Butyltin tris (2-ethylhexylthio-glycolate)	~20 %
		2) Di-n-butyltin bis (2-ethylhexylthio-glycolate)	~70%
	Tinstab BM270	1) Di-n-butyltin bis (methylmaleate)	~95%
Shell	Epoxy 828		~100%
Goldschmidt	Ortegol AO1	Steric hindered phenol derivate	66.7%
		Alkylated diphenylamine	33.3%
	Ortegol AO5	Steric hindered phenol derivate	70-72%
		Alkylated diphenylamine	20-22%
Crompton	Mark CZ 400 (Ca/Zn stabilizer)	2-(2-Butoxyethoxy)ethanol	<10%
		Alkylarylphosphites	55-65%
		Calcium 4-(1,1-dimethylethyl)benzoate	<10%
	Mark CZ 118S (Ca/Zn stabilizer)	Tris(nonylphenyl)phosphite	30-40%
		Other components - not listed	
	Mark BZ 592 (Ba/Zn stabilizer)	Solvent naphta, light aromatic	<10%
		Barium compounds	35-45%
		Triisodecyl phosphite	<25%

Table III - Composition of ingredients used as antiscorch materials (cnt'd)

Producer	Name	Ingredients	State
Crompton	Mark BZ 562 (Ba/Zn stabilizer)	Solvent naphta, light aromatic <10%	Liquid
		Alkylarylphosphites 20-30%	
	Mark BZ 555 (Ba/Zn stabilizer)	Zinc bis(p-nonylphenolate) <3%	
		Barium compounds 35-45%	
		Tris(2-ethylhexylmercaptoacetate) phosphate 5-15%	
Crompton	Mark BZ 563 (Ba/Zn stabilizer)	Diisodecyl phenyl phosphite 25-35%	Liquid
		Solvent naphta, light aromatic 5-15%	
	Mark BZ 563 (Ba/Zn stabilizer)	Barium compounds 20-30%	
		Diisodecyl phenyl phosphite 30-50%	
		2-(2-Butoxyethoxy)ethanol <5%	
Crompton	Mark BZ 563 (Ba/Zn stabilizer)	Zinc bis(p-nonylphenolate) <5%	Liquid
		Barium compounds 20-30%	

Example 3 in Table I and Examples 3 and 4 in Table II, respectively, demonstrate that the use of a conventional antioxidant, i.e. a mixture of hindered phenols and alkylated diphenyldiamines, alone or together with an epoxy moiety, does not prevent scorch in a bromine-containing FR formulation. Epoxy alone, either as DGEBA or ESBO, are not effective either (Examples 4 in Table 1, and Examples 1 and 2 in Table II). However, addition of metallic salts of various organic acids, significantly improves the resistance to scorch of a polyurethane flexible foam formulation including a bromine-containing flame retardant (Examples 8, 9 - Table I, and Examples 5, 6 - Table II).

All the above description has been provided for the purpose of illustration, and is not intended to limit the invention in any way. Various

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modifications can be carried out in the method and system according to the invention, without departing from its spirit.